A Variation of the F-test for Determining Statistical Relevance of Particular Parameters in EXAFS Fits

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Abstract.
A general problem when fitting EXAFS data is determining whether particular parameters are statistically significant. The F-test is an excellent way of determining relevancy in EXAFS because it only relies on the ratio of the fit residual of two possible models, and therefore the data errors approximately cancel. Although this test is widely used in crystallography (there, it is often called a "Hamilton test") and has been properly applied to EXAFS data in the past, it is very rarely applied in EXAFS analysis. We have implemented a variation of the F-test adapted for EXAFS data analysis in the RSXAP analysis package, and demonstrate its applicability with a few examples, including determining whether a particular scattering shell is warranted, and differentiating between two possible species or two possible structures in a given shell.

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1. INTRODUCTION

When fitting EXAFS data, one often must decide whether adding parameters or otherwise changing the fitting model significantly improves the fit beyond simply comparing the goodness-of-fit parameters. Hamilton[1] proposed a method based on the statistical F-test which has been widely used by crystallographers and has been extended by Bacchi *et. al.*[2]. Although many authors[3–7] have previously utilized the F-test with EXAFS data and have noted the importance of such a statistical test, it is still rarely applied.

A number of possible scenarios can arise in EXAFS analysis where the F-test should be applied. In fitting data to theoretical standards, the parameters usually come in groups associated with scattering shells; in general there are at least three or more new parameters per shell, though often some are constrained. A common question when fitting EXAFS data is to ask whether adding another shell (which often includes the addition of multiple parameters) would significantly improve the fit. Alternatively, one might ask whether one of the included shells could be removed without significantly worsening the fit. Other scenarios include using additional parameters for a given scattering shell, such as a third cumulant[8], or comparing different fitting models.

Here we begin by describing the F-test, focusing on the methodology of Hamilton. We then give examples of its application on (1) a system where one determines the significance of an additional scattering shell, and (2) where one questions the local structure of a given shell.

2. METHOD

The F-test is generally used in statistics to determine if the standard deviations of two populations are equal. Equivalently,

$$F = \frac{\chi_1^2/\nu_1}{\chi_0^2/\nu_0} \tag{1}$$

(where χ_0^2 represents the statistical χ^2 of the better fit (i.e. $\chi_0^2 < \chi_1^2$ and the ν_i represent the degrees of freedom in each case). It can be shown[9] that F in Eqn. 1 follows the F-distribution law. In other words, if the experimental value of F is denoted as F_{exp}, then the probability that F > F_{exp} gives the significance level at which the null hypothesis (that the two fits are not significantly different) can be rejected. A small value implies a very significant rejection in turn implying high confidence in the hypothesis that the fit that yields χ_0^2 is significantly better fit than the fit that yields χ_1^2. In this paper, we report α (Eqn. 6) as the confidence level that the χ_0^2 fit is the correct fit.

Equation 1 gives the general formula for the F-Test in statistics. In EXAFS analysis, however, it is generally preferable to test the variation of χ^2 versus the best fit (See Eqn. 2) in order to account for the possibility that some of the parameters in the two fits may be the same.

$$F = \frac{(\chi_1^2 - \chi_0^2)/(\nu_1 - \nu_0)}{\chi_0^2/\nu_0}. \tag{2}$$

Though one can immediately see that this equation cannot be applied when $\nu_0 = \nu_1$, i.e. when the number of fit parameters are the same in the two fits. In that case,

Michalowicz[5] suggests that one should use Eqn. 1 and notes that when the number of fit parameters is changed, the two equations produce the same qualitative answer but the calculated probabilities are different.

Hamilton[1] avoided this problem by introducing the *dimension* of the hypothesis, b, which is defined either as the difference in the degrees of freedom in the two cases ($b = \nu_1 - \nu_0$) or as the number of parameters that are changed (see examples). Thus, in Hamilton's variation, the ratio of the crystallographic R-factors ($\Re = R_1/R_0$, where R_0 and R_1 are the R-factors for the original (best) fit and the test fit, respectively,) are used in an F-test with n independent data points, m fit parameters (thus, $n-m$ degrees of freedom) and dimension of the hypothesis, b,

$$F = \frac{(R_1^2 - R_0^2)/b}{R_0^2/(n-m)} = \left[\left(\frac{R_1}{R_0}\right)^2 - 1\right]\frac{(n-m)}{b}. \quad (3)$$

The R-factor used by `rsfit`, the fitting program in the EXAFS analysis package RSXAP[10] is given by

$$R = \sqrt{\frac{\sum_i(\Delta(k^n\chi^R(r_i)))^2 + \sum_i(\Delta(k^n\chi^I(r_i)))^2}{\sum_i(k^n\chi_D^R(r_i))^2 + \sum_i(k^n\chi_D^I(r_i))^2}} * 100 \quad (4)$$

where $\Delta(k^n\chi(r))$ is the difference between the data and the standard function (calculated by the FEFF code[11]), and the R and I superscripts refer to the real and imaginary parts of the Fourier transform. If two fitting models use the same transform window, then the denominator in Eqn. 4 will be equal and cancel when this R-factor is used in the F-test as described by Hamilton (Eqn. 3). Assuming the data errors are roughly constant as a function of r, the ratio R_1/R_0 using this definition of the R-factor (Eqn. 4) is nearly proportional to $\sqrt{\chi_1^2/\chi_0^2}$ in Eqns. 1 and 2. It is worth pointing out that the R-factor calculated by `rsfit` (Eqn. 4) compares the data and the fit in r-space. This is equivalent to comparing them in k-space (as other fitting routines do) as long as one compares both the real and imaginary parts, independently, as is the case in `rsfit`. Furthermore, Hamilton[1] noted that the R-factor ratio R_1/R_0 is relatively insensitive to how the R-factors are defined. Thus, R_i^2 can be used in place of χ_i^2 in Eqns. 1 and 2, then Eqn. 3 is equivalent to Eqn. 2 where b is the difference in the number of parameters and $n-m$ is the degrees of freedom of the better fit.

From the hypothesis that there is no significant difference between two fits, Hamilton[1] tabulated a set of significance points, $\Re_{b,n-m,\alpha}$ defined by,

$$\Re_{b,n-m,\alpha} = \left(\frac{b}{n-m}\mathbf{F}_{b,n-m,\alpha} + 1\right)^{1/2} \quad (5)$$

where $\mathbf{F}_{b,n-m,\alpha}$ denotes the F-test analysis for a b-dimensional linear hypothesis with $n-m$ degrees of freedom Bacchi[2], *et. al.* have shown that the confidence level, α, that the fit that yields R_0 is a better fit than the fit that yields R_1 can be calculated by,

$$\begin{aligned}\alpha &= P(\Re > \Re_{b,n-m,\alpha}) \quad = \\ &\quad P(\mathbf{F} > \mathbf{F}_{b,n-m,\alpha}) \quad = \quad 1 - I_x[\frac{n-m}{2}, \frac{b}{2}], \quad (6)\end{aligned}$$

where P represents the probability, $I_x[\frac{n-m}{2}, \frac{b}{2}]$ is the incomplete beta function, $x = (\frac{(n-m)}{(n-m+bF)}) = (R_0/R_1)^2$, and F is given by Eqn. 3. For the R_0 fit to be considered a significantly better fit, α needs to be greater than 67% and preferably greater than 95%.

3. EXAMPLES

3.1. Adding an additional shell

The first example comes from a study of technetium (Tc) speciation in a cementitious nuclear waste form[12]. The Tc species formed is known to be a Tc sulfide, but the structure is not known with certainty. The data in this study are from 4 different samples with slightly different cement compositions, but all contain the same Tc species, TcS_x. The r-space data show a large peak at 1.9 Å with a shoulder at 2.1 Å, which correspond to 7 S and 2 Tc neighbors, at 2.38 and 2.77 Å, respectively. These distances and coordination numbers are typical of triangular cluster complexes of early transition elements (See Fig. 1: left)[13]. From this information, the structure of TcS_x can be seen to consist of triangular Tc disulfide clusters. The main question is whether the connectivity of these clusters can be determined with any certainty.

In addition to the big peak, the Fourier transform also contains three small features from 2.5 to 4.5 Å. It is known from the structure of the triangular "building block" that these features are due in part to scattering from S atoms. However, the features can be fit accurately using a combination of 6 S neighbors at 4.48 Å with $\frac{1}{3}$ Tc at 3.8 Å and $\frac{2}{3}$ Tc at 4.3 Å. These Tc distances correspond to Tc atoms connected through two bridging sulfide ligands and through a symmetrically bridging disulfide ligand, respectively (See Fig.1: right) The k-range for the Fourier transform was $2-13.3\text{Å}^{-1}$ and the r-range for the fit was $1-4.5$ Å; thus, the number of independent data points is 26.8 (given by Stern's[14] rule). The model containing only sulfide neighbors has 10 parameters and the model with both S and Tc neighbors has 14 parameters. For this study, the fit was performed using IFEFFIT[15]. The parameter "R-factor" in IFEFFIT is equivalent to R^2 in Eqn. 4 and is also weighted by an estimate of the noise in the spectrum. Therefore, the square root of the IFEFFIT parameter "R-factor" is given here as R.

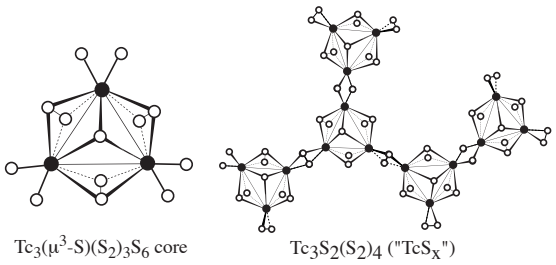

FIGURE 1. The core cluster (left), which corresponds to the 10 parameter model, and the connected structure (right), which corresponds to the 14 parameter model. Tc atoms are shown as solid circles and S atoms are shown as open circles.

When each data set is fit individually, the values for R_0 vary from 0.078 to 0.096 and the values for R_1 vary from 0.088 to 0.11. Using $n-m=12.8$ and $b=4$ in Eqn. 6 yields confidences of 35% to 82 % that the additional Tc atoms are present. In no case is the confidence >95%, and we cannot definitively conclude from this data that the additional Tc atoms are present. However, when one fits all four data sets simultaneously, there are 107.3 independent points, and $n-m=93.3$, $b=4$, $R_0=0.102$, and $R_1=0.113$. Due to the much larger number of degrees of freedom, fitting the data in this way gives a 99.9% confidence that the fit that includes the 2 additional Tc atoms is a better fit than the fit without them.

3.2. Substituting a shell

The second example comes from a study of ZnS:Cu,Cl and Zn:Cu,Mn,Cl devices which electroluminesces when an AC voltage is applied. This luminescence is strongly dependent on the Cu/Mn and Cl dopants, which has prompted an EXAFS analysis of the Cu and Mn K-edges on three different samples to understand their role.

The EXAFS analysis indicate that Mn substitutes for Zn in the ZnS lattice, i.e. the Mn K-edge data is fit very well with a ZnS structure. Cu, on the otherhand, appears to fit better with a CuS local structure for the nearest neighbor. The Hamilton test was applied to determine if the CuS structure gives a significantly better fit than ZnS structure (for comparison, see Fig. 2).

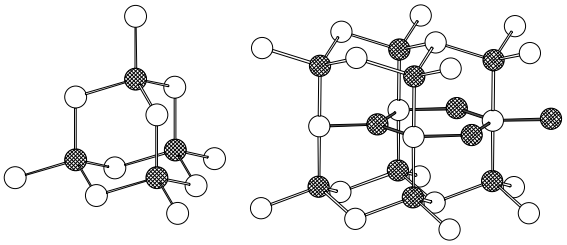

FIGURE 2. The structures of ZnS (left) and CuS (right). The S atoms are shown as white circles, Zn (left) or Cu (right) atoms are shaded. Note the two distinct Cu sites in the CuS structure (3-fold and 4-fold coordinated).

The fit to the CuS standard with four parameters yields an R-factor of 2.95. The fit to the ZnS standard, also with four fit parameters, yields an R-factor of 6.73. The k-range for the Fourier transform was $3-11.5$ Å^{-1}, and the r-range for the fit was $1.6-2.5$ Å, which gives 2.87 degrees of freedom using Stern's[14] rule. In this case, the dimension, b, of the hypothesis is the number of fit parameters. Thus, using $R_0=2.95$, $R_1=6.73$, $n-m=2.87$ and $b=4$ in Eqn. 6 yields an 80% confidence in the CuS structure. However, if we take into account all three samples simultaneously (similar to Example 1), it increases to a 99.9% confidence that the CuS structure is the correct environment for the Cu atoms.

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